AD-A103 998 OAKLAND UNIV ROCHESTER MICH F/G 12/1

TAYLOR-LAPLACE EXPANSIONS OF THE YUKAWA AND RELATED POTENTIAL E--ETC(U)

AUG 81 J M MCKINLEY, P P SCHMIDT N00014-77-C-0293

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OFFICE OF NAVAL RESEARCH

Contract No. N00014-77-C-0239

Task No. NR 359-648

Technical Report No. 7

(14) TR-7

Taylor-Laplace Expansions of the Yukawa and Related Potential Energy Functions

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Prepared for Publication in the
J. Phys. A (Math Phys.)

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1 August 1981

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SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

REPORT DOCUMENTATION PAGE

READ INSTRUCTIONS BEFORE COMPLETING FORM

1. REPORT NUMBER: 7	2. GOVT ACCESSION NO.: AD-A103 998	3. RECIPIENT'S CATALOG NUMBER
4. TITLE (and Subtitle): Taylor-Laplace Expansions of the Yukawa and Related Potential Energy Functions		5. TYPE OF REPORT & PERIOD COVERED: Technical 5/1/81 to 4/31/82
		6. PERFORMING ORG. REPORT NUMBER
7. AUTHOR(s): J. M. McKinley, P. P. Schmidt		8. CONTRACT OR GRANT NUMBER(s): N00014-77-C-0239
9. PERFORMING ORGANIZATION NAME AND ADDRESS: Departments of Physics and Chemistry, Oakland University, Rochester, Michigan 48063		10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS: NR 359-648
11. CONTROLLING OFFICE NAME AND ADDRESS		12. REPORT DATE: 8/1/81
		13. NUMBER OF PAGES: 24
14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office)		15. SECURITY CLASS. (of this report)
		15a. DECLASSIFICATION DOWNGRADING SCHEDULE

16. DISTRIBUTION STATEMENT (of this Report)

Approved for Public Release
Distribution Unlimited

17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)

18. SUPPLEMENTARY NOTES

Submitted to J. Phys. A (Math Phys.)

19. KEY WORDS (Continue on reverse side if necessary and identify by block number)

Taylor and Laplace series, Potential energy functions

20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

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Taylor-Laplace Expansions of the Yukawa and Related Potential Energy Functions

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Abstract

In the previous paper, we presented a general expression for the Taylor series for any function which can be expressed as a simple product of a purely radial and purely angular part. In this paper we apply that form of the Taylor series to the Yukawa potential [$y(r) = e^{-ar}/r$], and to several potential functions which can be derived from it. In particular, we examine the expansion of the Yukawa potential itself. In the limit as the exponent a vanishes, the Yukawa potential transforms into the Coulomb potential. We show that the limiting process applied to the Taylor series for the Yukawa potential yields the familiar form of the Laplace expansion of the Coulomb potential. Differentiation of the Yukawa potential with respect to the exponent a yields the exponential function. Hence, we develop a Taylor-Laplace power series representation of the Morse potential. Integration of the Yukawa potential with respect to the exponent, in the sense of the Laplace transform, yields functions of the form r^{-q}. Thus, Taylor series for the Lennard-Jones and related potentials can be constructed. Finally, we consider a Laplace-like functional expansion of the Yukawa potential followed by a Taylor series development about the end-point of a vector in the expansion. This process illustrates the application of the general methods to a more complicated angular dependence than one finds with the use of simple scalar functions. An appendix contains a Taylor series for one additional potential which is not directly related to the Yukawa potential: the Woods-Saxon potential. The expansion for the Buckingham exp-6 potential (totally derivable from the Yukawa potential) is also given.

1. Introduction

Given a general function $G(\underset{\sim}{r})$ of the vectorial separation between two points, $\underset{\sim}{r} = \underset{\sim}{r}_1 - \underset{\sim}{r}_2$, we can consider the expansion of this function in two ways. In one form of expansion, we can express the original function as a series of products of new functions. The arguments of the individual functions depend only upon components of $\underset{\sim}{r}_1$ or $\underset{\sim}{r}_2$ alone. Thus, the dependence on $\underset{\sim}{r}_1$ and $\underset{\sim}{r}_2$ in the original function is separated. The other form of expansion is to consider the development of the function as a power series in terms of the displacement(s) about the vectorial end-point(s). The Taylor series represents such a development.

In this paper we develop Taylor series for several commonly used potential energy functions. The functions all can be derived from the Yukawa potential function:

$$y(\underset{\sim}{r}) = \exp(-ar)/r. \tag{1.1}$$

The particular functions we consider in addition to the Yukawa potential are the Coulomb potential (we show this as a limiting form), the exponential and Morse potentials, and the Lennard-Jones potential. Included is the Buckingham exp-6 potential which is merely a hybrid form of terms which we consider. Our analysis shows that for parent functions which can be expressed as inverse powers, the Taylor series is equivalent to the Laplace expansion of the same function.

An objective in seeking functional or power series expansions of various potential functions is to be able to simplify the potential energy functions for complicated distributions of molecular sources.

Thus, given a spatial distribution of sources for a particular potential, e.g., electrostatic, exponential, Morse, or Lennard-Jones, it is frequently necessary to consider some form of symmetry-adapted expansion. Briels (1980) has considered this type of problem for functional expansions of the Buckingham (1938) exp-6 potential. In a number of instances, it is necessary to consider symmetry-adapted Taylor series as well. Schmidt, Pons and McKinley (1980) considered such an expansion in an analysis of the vibrations of ions and atoms in condensed phases. The formulae we consider here simplify the problem of constructing Taylor series.

In the next section we list the formulae needed for the subsequent discussion. In section 3 we consider the Taylor series for the Yukawa potential. In section 4 we consider the limiting transitions to the Coulomb, exponential, and Lennard-Jones potentials. Finally, in section 5 we consider the Laplace functional expansion of the Yukawa potential and the development of a Taylor series for one of the functional elements. The Woods-Saxon (1954) and Buckingham (1938) exp-6 potentials are considered briefly in an appendix.

2. The General Taylor Series

In the preceeding paper (McKinley and Schmidt, 198_) we showed that for any function $G(\underset{\sim}{r})$ which is separable into purely radial and angular parts of the form

$$G(\underset{\sim}{r}) = Y_{\lambda\mu}(\hat{r})F(r) \tag{2.1}$$

where $Y_{\lambda\mu}(\hat{r})$ is the spherical harmonic function, the Taylor series in terms of the vectorial displacement $\underset{\sim}{c}$ is

$$G(\underset{\sim}{r}+\underset{\sim}{c}) = (4\pi)^{3/2} \sum_{n=0}^{\infty} (c^n/n!) \sum_{L,M,\ell,m} (-i)^{L+n} A_{n\ell} Y_{LM}(\hat{r}) Y_{\ell m}(\hat{c})$$

$$\times \left\{\frac{(2L+1)}{(2\ell+1)(2\lambda+1)}\right\}^{1/2} (L\ell 00|\lambda 0)(L\ell Mm|\lambda\mu) I_{nL}(r). \qquad (2.2)$$

In this formula $(L\ell Mm|\lambda\mu)$ is the Clebsch-Gordan coefficient (Rose, 1957). $A_{n\ell}$ is given by (Morse and Feshback, 1953)

$$A_{n\ell} = \begin{cases} 0 & \text{for } \ell > n \text{ and } n - \ell \text{ odd} \\ \dfrac{(2\ell+1)n!(n-\ell+1)!!}{(n-\ell+1)!(n+\ell+1)!!} & \text{for } \ell \leq n \text{ and } \ell - n \text{ even} \end{cases} \qquad (2.3)$$

and $I_{nL}(r)$ is defined by

$$I_{nL}(r) = \frac{1}{(2\pi)^3} \int_0^\infty dk\ k^{n+2} f(k) j_L(kr) \qquad (2.4)$$

where $j_n(x)$ is the spherical Bessel function of the first kind (Arfken, 1970). The quantity $f(k)$ is

$$f(k) = 4\pi i^\lambda \int_0^\infty dr\ r^2 F(r) j_\lambda(kr). \qquad (2.5)$$

Equation (2.2) and the supporting equations (2.3)-(2.5) are used in the following sections.

We shall have need to use the limiting form of eqn (2.2) for a scalar function G: $\lambda = \mu = 0$. This quantity was derived in the preceeding paper (McKinley and Schmidt, 198_)

$$G_0(\underset{\sim}{r}) = \sqrt{4\pi}\sum_{n=0}^{\infty}(c^n/n!)\sum_{\ell}(-i)^{\ell+n}A_{n\ell}P_\ell(\hat{r}\cdot\hat{c})I_{n\ell}(r). \qquad (2.6)$$

$P_\ell(x)$ is the Legendre Polynomial.

3. Functional and Power Series for the Yukawa Potential

We now express the Yukawa potential, eqn (1.1), as

$$y(\underset{\sim}{r}) = \sqrt{4\pi}Y_{00}(\hat{r})\frac{1}{r}\exp(-ar). \qquad (3.1)$$

The Fourier transform is

$$f(k) = (4\pi)^{3/2}\int_0^\infty dr\ r\ \exp(-ar)j_0(kr)$$

$$= (4\pi)^{3/2}k^{-1}\int_0^\infty dr\ \exp(-ar)\sin(kr)$$

$$= (4\pi)^{3/2}\ \frac{1}{k^2 + a^2}\ . \qquad (3.2)$$

The radial factor, $I_{n\ell}(r)$, in the general term of the Taylor series is

$$I_{n\ell}(r) = \frac{1}{\pi^{3/2}}\int_0^\infty dk\ k^{n+2}\ \frac{1}{k^2 + a^2}\ j_\ell(kr) \qquad (3.3)$$

The integral can be evaluated in the upper half of the complex plane. The entire integrand is even (because $n - \ell$ is even). Thus the range is doubled to include the entire real axis of k. We now introduce the spherical Hankel functions with the use of

$$j_\ell(kr) = \text{Re}\ h_\ell^{(1)}(kr) \tag{3.4}$$

[as is customary, Re stands for the 'real part of']. The factor k^{n+2} in (3.3) removes the pole of order $\ell+1$ in $h_\ell^{(1)}(kr)$ at $k=0$. Thus, the only poles in the integrand are located at the points $k=\pm ia$. As a result, the integration yields modified spherical Bessel functions of the third kind (Arfken, 1970) which are defined by

$$k_\ell(ar) = i^{\ell+2} h_\ell^{(1)}(iar). \tag{3.5}$$

Altogether, we find

$$I_{n\ell}(r) = (4\pi)^{-1} a^{n+1} i^{n-\ell} k_\ell(ar).$$

The Yukawa potential at the displaced point now can be written as

$$y(\underset{\sim}{r}+\underset{\sim}{c}) = \sum_{n,\ell} \frac{(-c)^n}{n!} A_{n\ell} a^{n+1} P_\ell(\hat{r}\cdot\hat{c}) k_\ell(ar). \tag{3.6}$$

It is useful to compare this form of the expansion with a Laplace-type functional expansion of the same potential. [In section 5 we consider the Taylor expansion of part of the following functional form.] Given the Yukawa potential $y(r)$, eqn (3.1), we can consider the following relationship:

$$y(r_1-\underset{\sim}{r_2}) = \frac{1}{(2\pi)^3}\int d^3k\ \frac{4\pi}{k^2+a^2} \exp[-i\underset{\sim}{k}\cdot(\underset{\sim}{r_1}-\underset{\sim}{r_2})] \tag{3.7}$$

As is shown in section 5, with the use of two Rayleigh expansions for the exponential functions in eqn (3.7), the functional expansion is

$$y(\underset{\sim}{r}_1-\underset{\sim}{r}_2) = 4\pi\sum_{\lambda,\mu} a i_\lambda(ar_<)k_\lambda(ar_>)Y_{\lambda\mu}(\hat{r}_1)Y^*_{\lambda\mu}(\hat{r}_2) \qquad (3.8)$$

in which $i_n(x)$ is the modified spherical Bessel function of the first kind. The quantities $r_{>(<)}$ represent the greater (lesser) of r_1 and r_2. In this expression, apart from powers of r implicitly contained in the representations of the transcendental functions k_n and i_n as infinite power series, there is no explicit dependence on the powers of r_1 or r_2. The functional expansion is therefore distinctly different from the Taylor series. The angular dependence, expressed through the Legendre polynomials, is the only similarity between the two expressions.

4. Potentials Derived from the Yukawa Potential and its Taylor Series

In the Yukawa potential y(r), in the limit as a tends to zero we recover the Coulomb potential:

$$\lim_{a\to 0} \frac{e^{-ar}}{r} = 1/r. \qquad (4.1)$$

Differentiation of the Yukawa potential with respect to the exponential coefficient a yields the simple exponential function:

$$-\frac{d}{da}\frac{e^{-ar}}{r} = e^{-ar}. \qquad (4.2)$$

And, finally, when the Yukawa potential is part of the following integral

$$\frac{1}{(q-2)!}\int_0^\infty da\ a^{q-2}\ \frac{e^{-ar}}{r} = \frac{1}{r^q} \tag{4.3}$$

we recover functions of the form r^{-q}.

In this section we consider these three basic limiting cases and the Taylor series which can be derived from the indicated limiting processes.

The Coulomb potential is an appropriate limit of the Yukawa potential, as indicated above. When this limit is applied to the series representation (3.6), we obtain the following:

$$\begin{aligned}\frac{1}{|\underset{\sim}{r}+\underset{\sim}{c}|} &= \lim_{a\to 0} v(\underset{\sim}{r}+\underset{\sim}{c}) \\ &= \sum_{n,\ell}\frac{(-c)^n}{n!}\,A_{n\ell}\lim_{a\to 0}\{a^{n+1}k_\ell(ar)\}P_\ell(\hat{c}\cdot\hat{r}).\end{aligned} \tag{4.4}$$

From the definition of the modified spherical Bessel function (Arfken, 1970),

$$\lim_{a\to 0} k_\ell(ar) = \lim_{a\to 0}\frac{(2\ell)!}{2^\ell \ell!(ar)^{\ell+1}} = \lim_{a\to 0}\frac{(2\ell-1)!!}{(ar)^{\ell+1}} \tag{4.5}$$

so that

$$\lim_{a\to 0}[a^{n+1}k_\ell(ar)] = \delta_{n,\ell}\,\frac{1}{r^{\ell+1}}\,(2\ell-1)!!. \tag{4.6}$$

From eqn (2.3) which defines the coefficients $A_{n\ell}$, we find

$$A_{\ell\ell} = \frac{\ell!}{(2\ell-1)!!} \; . \tag{4.7}$$

Upon the substitution of eqn (4.6) and (4.7) into (3.6), we obtain

$$\frac{1}{|\underset{\sim}{r}+\underset{\sim}{c}|} = \sum_{\ell} \frac{(-c)^{\ell}}{r^{\ell+1}} P_{\ell}(\hat{r}\cdot\hat{c}) \tag{4.8}$$

which is identical to the Laplace expansion of the Coulomb potential.

We note that if a similar analysis is carried out with the use of eqn (4.22) of the preceeding paper (McKinley and Schmidt, 198_), we recover the Carlson-Rushbrooke (1950) expansion in the limit as the quantity a vanishes.

The simple exponential function exp(-ar) has been in use for a considerable time as a representation of the repulsive interactions which operate between atoms, ions, and molecules (Born and Mayer, 1932). Combinations of the exponential repulsion and inverse powers of attraction are commonly used in the analysis of intermolecular interactions (Hirschfelder, et al., 1954, Margenau and Kestner, 1969). A combination of exponential functions defines the Morse (1929) potential:

$$M(\underset{\sim}{r}) = D\, e^{a(r_0-r)}[e^{a(r_0-r)} - 2] \tag{4.9}$$

in which D is an energy of dissociation, and r_0 is an equilibrium separation. Briels (1980) has considered the functional expansion of the exponential component of the Buckingham exp-6 potential in order to develop symmetry-adapted series.

The Taylor series for the exponential function is

$$\exp[-a(r+c)] = -\frac{d}{da}\frac{\exp[-a(r+c)]}{|\underset{\sim}{r}+\underset{\sim}{c}|}$$

$$= -\sum_{n,\ell}\frac{(-c)^n}{n!}A_{n\ell}P_\ell(\hat{r}\cdot\hat{c})\frac{d}{da}[a^{n+1}k_\ell(ar)]. \tag{4.10}$$

With the use of the mixed recurrence relation (Abramowitz and Stegun, 1965)

$$zk_\ell'(z) = -zk_{\ell-1}(z) - (\ell+1)k_\ell(z) \tag{4.11}$$

in eqn (4.9), we get

$$\exp[-a(r+c)] = \sum_{n,\ell}\frac{(-ac)^n}{n!}A_{n\ell}P_\ell(\hat{r}\cdot\hat{c})[ark_{\ell-1}(ar) - (n-\ell)k_\ell(ar)]. \tag{4.12}$$

The Morse potential expands as

$$M(\underset{\sim}{r}+\underset{\sim}{c}) = D\sum_{n,\ell}\frac{(-ac)^n}{n!}A_{n\ell}P_\ell(\hat{r}\cdot\hat{c})\{2^n e^{2ar_0}[2ar\ k_{\ell-1}(2ar) \tag{4.13}$$

$$-(n-\ell)k_\ell(2ar)] - 2\ e^{ar_0}[ar\ k_{\ell-1}(ar) - (n-\ell)k_\ell(ar)]\}.$$

Finally, we consider the Taylor series for $|\underset{\sim}{r}+\underset{\sim}{c}|^{-q}$. Substituting the Taylor series for the Yukawa potential (3.6) into (4.3), we obtain

$$\frac{1}{|\underset{\sim}{r}+\underset{\sim}{c}|^q} = \frac{1}{(q-2)!}\int_0^\infty da\ a^{q-2}\sum_{n,\ell}\frac{(-c)^n}{n!}A_{n\ell}P_\ell(\hat{r}\cdot\hat{c})a^{n+1}k_\ell(ar)$$

$$= \frac{1}{(q-2)!}\sum_{n,\ell}A_{n\ell}\frac{(-c)^n}{n!}P_\ell(\hat{r}\cdot\hat{c})\int_0^\infty da\ a^{q+n-1}k_\ell(ar) \tag{4.14}$$

where we have exchanged the order of summation and integration. We now can use the mixed exponential-polynomial form of the modified spherical Bessel function (Abramowitz and Stegun, 1965)

$$k_\ell(x) = \frac{e^{-x}}{x} \sum_{s=0}^{\ell} \frac{(\ell+s)!}{(2s)!!\,(\ell-s)!} x^{-s} \tag{4.15}$$

to write

$$\int_0^\infty da\; a^{q+n-1} k_\ell(ar) = \frac{1}{r} \sum_{s=0}^{\ell} \frac{(\ell+s)!}{(2s)!!(\ell-s)!} \frac{1}{r^s} \int_0^\infty da\; a^{q+n-s-2} e^{-ar} . \tag{4.16}$$

The integral is uncomplicated and straightforward to evaluate as long as $q \geq 2$. [Note, from eqn (4.14) the expansion vanishes for $(q-2)<0$ because the factorial becomes infinite.] Thus, the expansion is

$$\frac{1}{|\underset{\sim}{r}+\underset{\sim}{c}|^q} = \frac{1}{r^q} \sum_{n,\ell,s} \Lambda_{n\ell} P_\ell(\hat{r}\cdot\hat{c}) \frac{(\ell+s)!(q+n-s-2)!}{n!(\ell-s)!(2s)!!\,(q-2)!} (-c/r)^n \tag{4.17}$$

It is interesting to note that this form is equivalent to the result obtained by Briels (1980) who used a functional expansion.

5. Laplace and Laplace-Taylor expansions of the Yukawa potential

The main problem we consider in this section concerns the evaluation of the Taylor series expansion of the function $y(\underset{\sim}{r}_1-\underset{\sim}{r}_2)$ about the point $\underset{\sim}{r}_1$. Such an expansion is required, for example, when one needs to consider a source at $\underset{\sim}{r}_2$ and the displacement of a particle about the point $\underset{\sim}{r}_1$; both points $\underset{\sim}{r}_1$ and $\underset{\sim}{r}_2$ share a common origin.

Before we consider the displacement about $\underset{\sim}{r}_1$ by $\underset{\sim}{c}$ in detail, we first demonstrate eqn (3.8), the Laplace functional expansion of the Yukawa potential.

The Fourier transform is given by eqn (3.2) together with $Y_{00}(\hat{k})$:

$$\text{F.t.}\{y(\underset{\sim}{r})\} = \frac{4\pi q}{k^2+a^2} \tag{5.1}$$

where here q is the strength of the source. The functional form of $y(\underset{\sim}{r}_1-\underset{\sim}{r}_2)$ is

$$y(\underset{\sim}{r}_1-\underset{\sim}{r}_2) = \frac{1}{(2\pi)^3}\int d^3k\,\frac{4\pi q}{k^2+a^2}\,\exp[-i\underset{\sim}{k}\cdot(\underset{\sim}{r}_1-\underset{\sim}{r}_2)]. \tag{5.2}$$

The use of two Rayleigh expansions

$$\exp(i\underset{\sim}{k}\cdot\underset{\sim}{r}) = 4\pi\sum_{\lambda,\mu} i^\lambda Y^*_{\lambda\mu}(\hat{r})Y_{\lambda\mu}(\hat{k})j_\lambda(kr) \tag{5.3}$$

in eqn (5.2) yields

$$y(\underset{\sim}{r}_1-\underset{\sim}{r}_2) = 8q\sum_{\lambda,\mu} Y_{\lambda\mu}(\hat{r}_1)Y^*_{\lambda\mu}(\hat{r}_2)\int_0^\infty dk\,\frac{k^2}{k^2+a^2}\,j_\lambda(kr_1)j_\lambda(kr_2) \tag{5.4}$$

upon integrating over the angles.

The radial integral is

$$I(r_1,r_2) = \int_0^\infty dk\,\frac{k^2}{k^2+a^2}\,j_\lambda(kr_1)j_\lambda(kr_2). \tag{5.5}$$

The evaluation of this integral proceeds along lines similar to the evaluation of eqn (3.3). We write

$$I = \tfrac{1}{2}\mathrm{Re}\int_{-\infty}^{\infty} dk\ \frac{k^2}{k^2+a^2}\, h_\lambda^{(1)}(kr_>)\,j_\lambda(kr_<) \tag{5.6}$$

in which $r_>$ is the greater of r_1, r_2. The $(\lambda+1)$-order pole in $h_\lambda^{(1)}$ at $k=0$ is removed by the $(\lambda+2)$-order zero in $k^2 j_\lambda(kr_<)$. Hence, closing the contour above, the only pole is at $k=+ia$. The integral I is

$$I = \tfrac{\pi}{2} a\, i_\lambda(ar_<)\,k_\lambda(ar_>). \tag{5.7}$$

Thus, the Laplace expansion of the Yukawa potential is that given by eqn (3.8):

$$y(\underset{\sim}{r}_1-\underset{\sim}{r}_2) = 4\pi q \sum_{\lambda\mu} Y_{\lambda\mu}(\hat{r}_1)\,Y^*_{\lambda\mu}(\hat{r}_2)\,a\,i_\lambda(ar_<)\,k_\lambda(ar_>). \tag{3.8}$$

We now consider the expansion about the point $\underset{\sim}{r}_1$:

$$y(\underset{\sim}{r}_1+\underset{\sim}{c}-\underset{\sim}{r}_2) = q \sum_{n=0}^{\infty} \frac{1}{n!}(\underset{\sim}{c}\cdot\underset{\sim}{\nabla}_1)^n\, y(\underset{\sim}{r}_1-\underset{\sim}{r}_2)$$

$$= 4\pi q \sum_{n\lambda\mu} \frac{1}{n!} Y^*_{\lambda\mu}(\hat{r}_2)\,(\underset{\sim}{c}\cdot\underset{\sim}{\nabla}_1)^n\,[Y_{\lambda\mu}(\hat{r}_1)\,a\,i_\lambda(ar_<)\,k_\lambda(ar_>)]. \tag{5.8}$$

In order to evaluate this expansion, we need to consider the 'partial potential'

$$\phi_\lambda(\underset{\sim}{r}_1) = Y_{\lambda\mu}(\hat{r}_1)\,a\,i_\lambda(ar_<)\,k_\lambda(ar_>)$$

$$= \frac{1}{(2\pi)^3}\int d^3k\ f_\lambda(k)\,Y_{\lambda\mu}(\hat{k})\exp(-i\underset{\sim}{k}\cdot\underset{\sim}{r}_1) \tag{5.9}$$

where

$$f_\lambda(k) = 4\pi i^\lambda \int_0^\infty dr_1\ r_1^2 \phi_\lambda(r_1) j_\lambda(kr_1)$$

$$= 4\pi i^\lambda \left\{ \int_0^{r_2} dr_1 r_1^2 a i_\lambda(ar_1) k_\lambda(ar_2) j_\lambda(kr_1) + \int_{r_2}^\infty dr_1 r_1^2\ a i_\lambda(ar_2) k_\lambda(ar_1) j_\lambda(kr_1) \right\}. \tag{5.10}$$

We show in appendix 2 that

$$f_\lambda(k) = \frac{4\pi i^\lambda}{k^2+a^2} j_\lambda(kr_2). \tag{5.11}$$

In the standard manner, we now find

$$\frac{1}{n!}(\underset{\sim}{c}\cdot\underset{\sim}{\nabla})^n \phi_\lambda(\underset{\sim}{r_1}) = (4\pi)^{3/2} \frac{c^n}{n!} \sum_{\ell m L M} (-i)^{n+L} A_{n\ell} Y_{\ell m}(\hat{c}) Y_{LM}(\hat{r}_1)$$

$$\times \left\{ \frac{2L+1}{(2\lambda+1)(2\ell+1)} \right\}^{1/2} (L\ell 00|\lambda 0)(L\ell M m|\lambda\mu) I_{nL\lambda}(r_1) \tag{5.12}$$

where specifically,

$$I_{nL\lambda}(r_1) = \frac{1}{(2\pi)^3} \int_0^\infty dk\ k^{n+2} \frac{4\pi i^\lambda}{k^2+a^2}\ j_\lambda(kr_2) j_L(kr_1)$$

$$= \frac{i^\lambda}{2\pi^2} \int_0^\infty dk\ \frac{k^{n+2}}{k^2+a^2}\ j_\lambda(kr_2) j_L(kr_1). \tag{5.13}$$

From the parity of the Clebsch-Gordan coefficient, $\ell+L+\lambda$=even. From $A_{n\ell}$, $n-\ell$= even. Thus, $L+n+\lambda$=even. The integrand is even and can be doubled. Write

$$I_{nL\lambda}(r_1) = \frac{i}{4\pi^2}\int_{-\infty}^{\infty} dk \; \frac{k^{n+2}}{k^2+a^2} \; j_\lambda(kr_2)j_L(kr_1). \tag{5.14}$$

We consider two cases separately.

Case A: $r_1<r_2$. Let $j_\lambda(kr_2)$ = Re $h_\lambda^{(1)}(kr_2)$ and close the contour above. As $k\to 0$, the entire integrand behaves as $k^{n-\lambda+L+1}$. The The triangle inequality for the Clebsch-Gordan coefficient ensures that $\ell+L-\lambda\geq 0$. We know that $n-\ell\geq 0$. Thus, $n+L-\lambda\geq 0$, and there is no pole at k=0. The pole at k=ia contributes through its residue to the integral:

$$I_{nL\lambda}(r_1) = \frac{i^{n+L}}{4\pi} \; a^{n+1}k_\lambda(ar_2)i_\lambda(ar_1) \tag{5.15}$$

and

$$y(\underset{\sim}{r}_1+\underset{\sim}{c}-\underset{\sim}{r}_2)_{r_1<r_2} = (4\pi)^{3/2}q \sum_{n\lambda\mu\ell mLM}(c^n/n!)A_{n\ell}Y^*_{\lambda\mu}(\hat{r}_2)Y_{\ell m}(\hat{c})Y_{LM}(\hat{r}_1)$$

$$\times\left(\frac{2L+1}{(2\lambda+1)(2\ell+1)}\right)^{1/2}(L\ell 00|\lambda 0)(\ell LmM|\lambda\mu)a^{n+1}k_\lambda(ar_2)i_L(ar_1). \tag{5.16}$$

In the limit as $r_1\to 0$ in eqn (5.16), we recover eqn (3.6).

Case B: $r_1>r_2$. Proceed in a manner which is similar to case A. Let $j_L(kr_1)$ = Re $h_L^{(1)}(kr_1)$. Again, we can show that $n+\lambda-L\geq 0$ so that there is no pole at k=0. The residue at k=ia now yields

$$I_{nL\lambda}(r_1) = \frac{1}{4\pi} \; i^{n+2\lambda-1} \; a^{n+1}i_\lambda(ar_2)k_\lambda(ar_1) \tag{5.17}$$

and

$$y(\underset{\sim}{r}_1+\underset{\sim}{c}-\underset{\sim}{r}_2)_{r_1>r_2} = (4\pi)^{3/2}q \sum_{n\lambda\mu\ell mLM} (c^n/n!)A_{n\ell}Y^*_{\lambda\mu}(\hat{r}_2)Y_{\ell m}(\hat{c})Y_{LM}(\hat{r}_1)$$

$$\times\left[\frac{2L+1}{(2\lambda+1)(2\ell+1)}\right]^{1/2}(L\ell 00|\ell 0)(L\ell\ Mm|\lambda\mu)a^{n+1}i_\lambda(ar_2)k_L(ar_1). \quad (5.18)$$

As an example, we now apply these results to the problem of a ring of source, such as a charged ring or a ring of source for the Morse potential.

The distribution of source is such that an element of source dq is in the vicinity of $\underset{\sim}{r}_2$. Thus, we write

$$y(\underset{\sim}{r}_1) = \int dy(\underset{\sim}{r}_1-\underset{\sim}{r}_2)$$

$$= 4\pi\int dq \sum_{\lambda,\mu} Y_{\lambda\mu}(\hat{r}_1)Y^*_{\lambda\mu}(\hat{r}_2)\ ai_\lambda(ar_<)k_\lambda(ar_>). \quad (5.19)$$

For the case of a ring, the magnitude of r_2 is constant. Hence,

$$dq = \frac{q}{2\pi}\, d\phi_2 \quad (5.20)$$

and

$$\int dq\ Y^*_{\lambda\mu}(\hat{r}_2) = \frac{q}{2\pi}\int d\phi_2\left[\frac{2\lambda+1}{4\pi}\ \frac{(\lambda-\mu)!}{(\lambda+\mu)!}\right]^{1/2} P^\mu_\lambda(\cos\theta_2)e^{-i\mu\phi_2}$$

$$= q\ Y_{\lambda 0}(\hat{r}_2)\delta_{\mu 0}. \quad (5.21)$$

We find for $y(\underset{\sim}{r}_1)$

$$y(\underset{\sim}{r}_1) = qa\sum_\lambda i_\lambda(ar_<)k_\lambda(ar_>)(2\lambda+1)P_\lambda(\cos\theta_1)P_\lambda(\cos\theta_2) \quad (5.22)$$

We now use the results obtained above to investigate displacements by $\underset{\sim}{c}$ about $\underset{\sim}{r}_1$. For $r_1<r_2$ we have

$$y(\underset{\sim}{r}_1+\underset{\sim}{c})_{r_1<r_2} = (4\pi)^{3/2}q \sum_{n\lambda\mu\ell mLM} (c^n/n!)\Lambda_{n\ell}Y_{\lambda 0}(\hat{r}_2)Y_{LM}(\hat{r}_1)Y_{\ell m}(\hat{c})$$

$$\times\left[\frac{2L+1}{(2\lambda+1)(2\ell+1)}\right]^{1/2}(L\ell 00|\lambda 0)(L\ell Mm|\lambda 0)a^{n+1}i_L(ar_1)k_\lambda(ar_2) \quad (5.23)$$

and for $r_1>r_2$

$$y(\underset{\sim}{r}_1+\underset{\sim}{c}) = (4\pi)^{3/2}q \sum_{n\lambda\mu\ell mLM} \frac{(-c)^n}{n!}\Lambda_{n\ell}Y_{\lambda 0}(\hat{r}_2)Y_{LM}(\hat{r}_1)Y_{\ell m}(\hat{c})$$

$$\times\left[\frac{2L+1}{(2\lambda+1)(2\ell+1)}\right]^{1/2}(L\ell 00|\lambda 0)(L\ell Mm|\lambda 0)a^{n+1}i_\lambda(ar_2)k_L(ar_1). \quad (5.24)$$

In the limit as a tends to zero in these expressions, we recover the forms associated with the Coulomb potential:

$$\lim_{a\to 0} y(\underset{\sim}{r}_1) = q\sum_\lambda(2\lambda+1)P_\lambda(\cos\theta_1)P_\lambda(\cos\theta_2)\lim_{a\to 0} ai_\lambda(ar_<)k_\lambda(ar_>)$$

$$= q\sum_\lambda P_\lambda(\cos\theta_1)P_\lambda(\cos\theta_2)\ \frac{r_<^\lambda}{r_>^{\lambda+1}} \quad (5.25)$$

from eqn (5.22). This expression usually is obtained as an example in classical electrostatics by other means (cf., Jackson, 1962, p.64).

The Coulomb limit for the expansions (5.23) and (5.24) yields

$$\lim_{a\to 0} y(\underset{\sim}{r}_1+\underset{\sim}{c}-\underset{\sim}{r}_2)_{r_1<r_2} = (4\pi)^{3/2}q \sum_{\ell Lm} \frac{c^\ell}{\ell!}Y_{L+\ell,0}(\hat{r}_2)Y_{L,-m}(\hat{r}_1)Y_{\ell m}(\hat{c})$$

$$\times\left(\frac{2L+1}{(2\ell+1)(2L+2\ell+1)}\right)^{1/2}(L\ell 00|L+\ell 0)(L\ell\text{-}mm|L+\ell 0)\frac{(2L+2\ell-1)!!}{(2L+1)!!}$$

$$\times\frac{r_1^L}{r_2^{L+\ell+1}} \qquad (5.26)$$

and

$$\lim_{a\to 0} y(\underset{\sim}{r}_1+\underset{\sim}{c}-\underset{\sim}{r}_2)_{r_1>r_2} = (4\pi)^{3/2} q \sum_{\ell L m} \frac{(-c)^\ell}{\ell!} Y_{\ell-L,0}(\hat{r}_2) Y_{L,-m}(\hat{r}_1)$$

$$\times Y_{\ell m}(\hat{c})\left(\frac{2L+1}{(2\ell+1)(2\ell-2L+1)}\right)^{1/2}(L\ell 00|\ell-L0)(L\ell\text{-}mm|\ell-L0)$$

$$\times\frac{(2L-1)!!}{(2\ell-2L+1)!!}\;\frac{r_2^{\ell-L}}{r_1^{L+1}}\;. \qquad (5.27)$$

Although we have examined the case of the ring as an example, it is far from an idle one. There are numbers of systems of interest in physics, chemistry, and biology in which essentially one atom or ion sits in close proximity to a configuration of atoms which are bound together as pentagons, hexagons, and higher regular polygons. Some examples are the single crystal surfaces of pure, clean metals and other solids, annular, charged ring molecules in chemistry, and surface aggregates of phosphate ions in biological membranes. It is easy to show by computer simulation (Schmidt, unpublished) that the difference between the hexagon and a continuous ring is a small one. Thus, the ring of charge or matter as the source density for the Morse potential, for example, serves a useful function. The analyses of vibrations and stabilities in such systems are facilitated by the analyses given above.

Appendix I. The Woods-Saxon and Buckingham exp-6 potentials

We have mentioned the Buckingham (1938) potential in the text of this paper. In this appendix we show a general expression for the Taylor series expansion of this potential. The result compliments Briels (1980) functional expansion. First, however, we consider a different kind of potential energy function, one which depends upon the exponential function, but is not directly related to the Yukawa potential. The function is the Woods-Saxon (1954) potential which has been used frequently in the analyses of nuclear models.

The Woods-Saxon potential has a simple form:

$$\phi_{WS} = \frac{-V_0}{1 + \exp[(r - r_0)/\rho]} \ . \tag{I.1}$$

This function does not easily admit a Fourier transform. Therefore, the direct application of the integral form of the Taylor series is inappropriate. We resort to a differential form (McKinley and Schmidt, 198_) in order to get useful results.

In particular, in the previous paper we showed that for a scalar function of the form

$$\begin{aligned} G(\underset{\sim}{r}) &= Y_{00}(\hat{r})[\sqrt{4\pi}F(r)] \\ &= F(r) \end{aligned} \tag{I.2}$$

an arbitrary term in the Taylor series is

$$\frac{1}{n!}(\underset{\sim}{c}\cdot\underset{\sim}{\nabla})^n F(r) = \frac{c^n}{n!}\sum_{\ell}\Lambda_{n\ell}P_\ell(\hat{r}\cdot\hat{c})\sum_{q=0}^{\ell}\frac{(-1)^q(\ell+q)!}{(\ell-q)!(2q)!!}\ r^{-q}\left(\frac{n-q}{r}\right.$$

$$+ \left.\frac{d}{dr}\right\} (d/dr)^{n-q-1} F(r). \qquad (I.3)$$

For the case of the Woods-Saxon potential, it is reasonably easy to obtain a closed, polynomial representation for the differentiations indicated in eqn (I.3).

The differentiation of the Woods-Saxon potential (I.1) to arbitrary order is carried out as follows. Let

$$x = \exp[(r-r_0)/\rho]. \qquad (I.4)$$

Then

$$(d/dr)^n = \rho^{-n}\left\{x\frac{d}{dx}\right\}^n \qquad (I.5)$$

and by means of mathematical induction we find

$$\left\{x\frac{d}{dx}\right\}^n = \sum_{s=1}^{n} C_s^n x^s (d/dx)^s \qquad (I.6)$$

where the coefficients C_s^n are determined by means of the following initial and end conditions

$$\begin{aligned} C_1^n &= C_n^n = 1 \\ C_s^n &= 0 \text{ for all } s > n \end{aligned} \qquad (I.7)$$

and the recursion relation

$$C_s^n = sC_s^{n-1} + C_{s-1}^{n-1}. \qquad (I.8)$$

The differentiation of the Woods-Saxon potential now leads to the general term for the Taylor expansion

$$\frac{1}{n!}(\underset{\sim}{c}\cdot\underset{\sim}{\nabla})^n\phi_{WS} = -\frac{V_0c^n}{n!\rho^n}\sum_{\ell}A_{n\ell}P_{\ell}(\hat{r}\cdot\hat{c})\sum_{q=0}^{\ell}\frac{(-1)^q(\ell+q)!}{(\ell-q)!(2q)!!}(\rho/r)^q$$

$$\times\left\{(n-q)(\rho/r)\sum_{s=1}^{n-q-1}C_s^{n-q-1}\;e(s) + \sum_{s=1}^{n-q}C_s^{n-q}\;e(s)\right\} \qquad (1.9)$$

in which $e(s)$ is

$$e(s) = (-1)^s\frac{\exp[s(r-r_0)/\rho]}{\{1+\exp[(r-r_0)/\rho]\}^s}\;. \qquad (1.10)$$

The Buckingham potential is simply a combination of the exponential and van der Waals r^{-6} potentials:

$$\phi_B(\underset{\sim}{r}) = ae^{-br} - c/r^6. \qquad (1.11)$$

The Taylor expansion of this function is just the combinations of eqn (4.12) and (4.17). We find specifically

$$\phi_B(\underset{\sim}{r}+\underset{\sim}{r}') = \sum_{n,\ell}\frac{(-r')^n}{n!}A_{n\ell}P_{\ell}(\hat{r}\cdot\hat{r}')\left\{ab^n[brk_{\ell-1}(br)-(n-\ell)k_{\ell}(br)]\right.$$

$$\left.-\frac{1}{24}\frac{c}{r^{n+6}}\sum_{s=0}^{\ell}\frac{(\ell+s)!(n+4-s)!}{(\ell-s)!(2s)!!}\right\}. \qquad (1.12)$$

Appendix II. The evaluation of the integral (5.10)

We evaluate the Fourier radial transform, eqn (5.10), as follows.

Write the spherical Bessel equation as

$$\frac{d}{dr}[r^2\frac{d}{dr}j_\lambda(kr)] + (kr)^2 j_\lambda(kr) - \lambda(\lambda+1)j_\lambda(kr) = 0. \qquad (II.1)$$

We write the modified spherical Bessel equation for any of its solutions as

$$\frac{d}{dr}[r^2\frac{d}{dr}\zeta_\lambda(\alpha r)] - (\alpha r)^2\zeta_\lambda(\alpha r) - \lambda(\lambda+1)\zeta_\lambda(\alpha r) = 0. \qquad (II.2)$$

Multiply the first equation by $-\zeta_\lambda(\alpha r)$ and the second by $j_\lambda(kr)$ and add:

$$-\zeta_\lambda(\alpha r)\frac{d}{dr}[r^2\frac{d}{dr}j_\lambda(kr)] + j_\lambda(kr)[r^2\frac{d}{dr}\zeta_\lambda(\alpha r)] - \zeta_\lambda(\alpha r)(kr)^2 j_\lambda(kr)$$
$$- j_\lambda(kr)(\alpha r)^2\zeta_\lambda(\alpha r) = 0 \qquad (II.3)$$

The first two terms are integrated by parts. The third and fourth terms are transposed. The result is

$$r^2\zeta_\lambda(\alpha r)j_\lambda(kr) = \frac{1}{k^2+\alpha^2}\frac{d}{dr}\left(j_\lambda(kr)r^2\frac{d}{dr}\zeta_\lambda(\alpha r) - r^2\zeta_\lambda(\alpha r)\frac{d}{dr}j_\lambda(kr)\right). \qquad (II.4)$$

When this result is substituted into eqn (5.10), we find

$$f_\lambda(k) = \frac{4\pi i^\lambda}{k^2+\alpha^2}\Big\{\alpha k_\lambda(\alpha r_2)[j_\lambda(kr_1)r_1^2\frac{d}{dr_1}i_\lambda(\alpha r_1) - r_1^2 i_\lambda(\alpha r_1)\frac{d}{dr_1}j_\lambda(kr_1)]_0^{r_2}$$

$$+ \alpha i_\lambda(\alpha r_2)[j_\lambda(kr_1)r_1^2\frac{d}{dr_1}k_\lambda(\alpha r_1) - r_1^2 k_\lambda(\alpha r_1)\frac{d}{dr_1}j_\lambda(kr_1)]_{r_2}^0\Big\}$$

$$= \frac{4\pi i^\lambda}{k^2+\alpha^2}\alpha^2 r_2^2 j_\lambda(kr_2)[k_\lambda(\alpha r_2)i_\lambda'(\alpha r_2) - i_\lambda(\alpha r_2)k_\lambda'(\alpha r_2)]. \quad (11.5)$$

The quantity in the brackets is a simple Wronskian which has the value $1/(\alpha^2 r_2^2)$ (Arfken, 1970). Thus,

$$f_\lambda(k) = \frac{4\pi i^\lambda}{k^2+\alpha^2}j_\lambda(kr_2). \quad (5.11)$$

Acknowledgement

This work was supported in part by the U. S. Office of Naval Research, Arlington, Virginia USA.

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